

Memorandum

To: Stephanie Vaughn, EPA Region 2

Elizabeth Buckrucker, USACE

From: Frank Tsang and Scott Kirchner

Date: October 31, 2014

Subject: 2013 Low Resolution Coring Second Supplemental Split Sample Data

Comparison for the Lower Passaic River Study Area

At the request of the United State Environmental Protection Agency (EPA) and the United States Army Corps of Engineers (USACE), CDM Federal Programs Corporation (CDM Smith) collected oversight split sediment samples as part of the Lower Passaic River (LPR) Restoration Project remedial investigation conducted by the Cooperating Parties Group (CPG). This memorandum presents the comparison of the EPA oversight team's split sample results to the CPG's sample results and discusses the differences in the data pairs. In this document, samples are referred to as either CPG samples or EPA split samples for clarity.

The split sample comparison consisted of 25 sample pairs, which were evaluated for dioxins/furans, pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), total organic carbon (TOC), and metals analysis. Thirty-two out of 48 compounds (67%) evaluated in the EPA and CPG split samples comparison are comparable. Only the 22 chemicals listed below are not comparable.

- <u>Dioxins/Furans</u>: 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin (1,2,3,4,6,7,8-HPCDD), 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), octachlorodibenzofuran (OCDF), total heptachlorodibenzo-p-dioxin (total HPCDD), and total tetrachlorodibenzo-p-dioxin (total TCDD)
- <u>Pesticides</u>: 2,4'-dichlorodiphenyltrichloroethane (2,4'-DDT), 4,4'-dichlorodiphenyltrichloroethane (4,4'-DDT), and dieldrin
- PCBs: 3,3',4,4'-tetrachlorobiphenyl (PCB 77), 3,3',4,4',5-pentachlorobiphenyl (PCB 126), 2,3,3',4,4',5-hexachlorobiphenyl (PCB 156) plus 2,3,3',4,4',5'-hexachlorobiphenyl (PCB 157), and total polychlorinated biphenyls (total PCBs)
- PAHs: anthracene, benzo(a)anthracene, fluoranthene, indeno(1,2,3-cd)pyrene, and pyrene
- Metals: cadmium, chromium, lead, and mercury
- Total Organic Carbon

Oversight Program

Oversight was conducted in accordance with the Final Quality Assurance Project Plan (QAPP), Addendum 10, Low Resolution Coring Supplemental Sampling for the Lower Passaic River Restoration Project (CDM Smith 2012). The split sample program consisted of 25 sediment split samples collected from the study area.

Data Comparison Methodology

The CPG and EPA split sample data were evaluated for potential differences by plotting selected analytes listed on Table 1. For each of the following three plots, data are plotted on the figures evaluated only for the cases where both sample pairs are detected.

- <u>Line Plot</u>: The concentrations measured by both analytical programs for the detected paired samples
 were plotted against the same axes. The graph depicts the relative magnitudes and patterns of
 concentrations.
- <u>Bivariate Scatter Plot</u>: CPG sample concentration was plotted as a function of EPA sample concentration for each detected pair. The bivariate scatter plot illustrates the relationship between EPA and CPG data. Also included on the graph is a line which depicts a 1:1 ratio of concentration of EPA and CPG sample. The bivariate scatter plot can be used to identify potential systematic bias when data points fall consistently above or below the 1:1 line.
- <u>Percent Difference Plot</u>: The percent difference (%D) was defined as the difference between concentration for detected data pairs, divided by the concentration of EPA sample (Equation 1).

%
$$D = \frac{(R_{EPA} - R_{CPG})}{(R_{EPA})}$$
 (100) (Equation 1)

Consequently, a negative %D indicates a CPG result that is higher than the EPA result, while a positive %D indicates a CPG result that is lower than the EPA result. This plot provides a visual indication of the extent of positive and negative differences between the two data pairs. The red dashed lines on the plot correspond to the criteria of 40%D and -67%D. These criteria correspond to 50% relative percent difference (RPD) (the CPG's field duplicate acceptance criterion), converted to %D values. The term of %D is commonly used when one of the two values is known or accepted, whereas RPD is more commonly used when both values are uncertain. The sample data in this graph was represented with the EPA result as the known value and the CPG result as the unknown value.

In addition to the preparation of data comparison plots on the figures, the tests described below were also conducted for CPG and EPA data pairs and presented in Table 1.

Average Ratio: The ratios of the CPG results to EPA results were calculated for each detected data pair. The average ratio and standard deviation were calculated for each compound. An average ratio above one indicates that the CPG results were detected higher than the EPA results, while an average ratio below one indicates that the CPG results were detected lower than the EPA results.



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- <u>Percent Difference</u>: The calculated %D values were evaluated against the acceptance criteria of greater than or equal to -67%, or less than or equal to 40% (equivalent to less than or equal to 50% RPD).
- <u>Statistical Test</u>: The statistical tests were performed to calculate *p*-values. The *p*-value is an indicator of the presence of a difference between the data pairs. A *p*-value of less than 0.05 indicates a statistically significant difference between the two data sets.
 - ☐ <u>Wilcoxon Signed Rank (WSR) Test</u>: The WSR test was used to calculate *p*-values for all detected sample pairs.
 - Paired Prentice-Wilcoxon (PPW) Test: The PPW test was performed to allow inclusion of the left-censored (nondetected) data pairs. The elimination of data pairs containing nondetected values is essentially equivalent to ignoring potentially substantial information contained within these nondetect-containing data pairs, and may lead to biased results. The PPW test relies on survival analysis computations as detailed in O'Brien and Fleming (1987) and is considered the standard test for the case of censored matched pairs (Helsel 2005).

The data comparison plots are depicted in Figures 1 through 48. Results for the three comparison criteria (average ratio, %D, and statistical tests) are presented in Table 1. The numbers of split sample pairs are listed for each compound along with the number of pairs which had detected results for both samples. The average ratio of results of CPG sample to those of EPA sample results are reported with the standard deviation of the ratios. The %D results are summarized by reporting the percentage of data pairs that exceeded the acceptance criteria (40% and -67%). Also included are the *p*-values calculated by the WSR test and the PPW test.

An overall evaluation of the split sample data is based on the result of the three comparison criteria, where each compound has a rating of "Same" or "Different". The data pairs are considered comparable or "Same" if at least two of the three criteria are met. The comparison criteria for each compound are listed below.

- Average Ratio: Average ratio of CPG to EPA results within 0.70 to 1.30.
- <u>Percent Difference</u>: Less than 16% of the data pairs exceed the acceptance criteria of -67% to 40%.
- Statistical Test (WSR Test and PPW Test): p-Values greater than or equal to 0.05 are within acceptance limits, indicating there is no significant statistical difference between the data sets. When WSR test and PPW test draw different conclusions:
 - The conclusions of the PPW test would be used for data sets that include nondetects since PPW test is capable of handling nondetects.
 - The conclusions of the WSR test would be used for data sets that include all detected sample pairs especially if potential outliers are present. The WSR test is much less sensitive to outliers compared to the PPW test.



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Results of data comparison of CPG and EPA split samples are summarized below and presented in Table 1 and Figures 1 through 48.

Dioxins/Furans

There were eight dioxin/furan compounds evaluated for the three comparison criteria. The data pairs for five compounds, 1,2,3,4,6,7,8-HPCDD, 2,3,7,8-TCDD, OCDF, total HPCDD, and total TCDD, were not comparable (Table 1). From examination of individual sample pairs, the calculated high average ratios were influenced by several high detections which differed greatly between these two data pairs. The majority of detections were within %D criteria as shown in Figures 1 through 8. The WSR and PPW tests results for 1,2,3,4,6,7,8-HPCDD and total HPCDD differed because there is a potential outlier (13B-0564-G2AS). If the sample pairs for 13B-0564-G2AS were removed from the data sets, the p-values for both WSR and PPW tests were less than 0.05. Therefore, the sample pairs are statistically different.

Pesticides

The data pairs for all pesticide compounds were comparable, except 2,4'-DDT, 4,4'-DDT, and dieldrin. The three compounds failed to meet %D criteria and PPW test (Table 1). Figures 9 through 16 show the data comparison plots for eight of the pesticide compounds evaluated. The WSR and PPW tests results for 4,4'-dichlorodiphenyldichloroethylene and alpha-chlordane differed probably because there is a potential outlier (13B-0564-G2AS). However, the conclusion from the PPW test is preferred over the WSR test because there are nondetects in the data sets. Therefore, these two compounds were considered as comparable.

Polychlorinated Biphenyls

Four of the eleven compounds evaluated by the three comparison criteria were found to be different in data pairs (Table1). They are PCB 77, PCB 126, PCB 156 plus PCB 157, and total PCBs. The majority of detections were within %D criteria. The bivariate scatter plots in Figures 17 through 27 show the predominant high bias of CPG results relative to EPA results. The total PCB results were also found to be different even though the PPW test p-value is slightly greater than 0.05. However, due to potential outlier, the conclusion from the WSR test is used.

Polycyclic Aromatic Hydrocarbons

Of the nine evaluated PAH compounds, anthracene, benzo(a)anthracene, fluoranthene, indeno(1,2,3-cd)pyrene, and pyrene were considered different in data pairs. All compounds failed to meet %D criterion as shown in Figures 28 through 36, but all compounds meet the average ratio criterion. The data pair for the five compounds was considered statistically different based on both WSR and PPW tests. The WSR and PPW tests results for anthracene differed because there is a potential outlier (13B-0531-C2CS). Therefore, the conclusion from the WSR test is used.

Metals

Split sample data was evaluated for eleven metals, and the results were found to be comparable, except for cadmium, chromium, lead, and mercury. Figures 37 through 47 show the statistical plots for metals.



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Cadmium and mercury did not meet the average ratio and %D comparison criteria. The data pair for cadmium and lead were considered statistically different based on both WSR and PPW tests. The WSR and PPW tests results for chromium and mercury differed because there is a potential outlier (13B-0564-G2AS). Therefore, the conclusion from the WSR test is used since it is less sensitive to outliers.

Two of the mercury results seem to be incorrectly labelled by the laboratory as 13B-0503-C2AS-C and 13B-0503-C3CS-C instead of 13B-0559-C2AS-C and 13B-0559-C3CS-C, respectively. Sample 13B-0503-C2AS-C has the same sample date and time as 13B-0559-C2AS-C. Therefore, it is concluded that these are the same sample. The same goes for 13B-0503-C3CS-C. The database is corrected based on this assumption. In addition, there is no EPA split sample result for mercury corresponding to sample 13B-0521-C3AS. There is an EPA mercury result for sample 13B-0521-C2AS-C. This sample was collected at the same station, same depth interval, but different core. For the split sample comparison, 13B-0521-C2AS-C sample is used as a split sample for 13B-0521-C3AS.

Total Organic Carbon

The results for TOC were not comparable for the two data pairs. The CPG data are usually much higher than the EPA data (Figure 48). The statistical tests also indicated that the data was statistically different.

Similar to mercury, there are no EPA split sample results for TOC corresponding to sample 13B-0530-C3AS and 13B-0530-C3BS. Instead, there are EPA samples 13B-0530-C4AS-C and 13B-0530-C4BS-C which were collected at the same station, same depth interval, but different core. For the split sample comparison, 13B-0530-C4AS-C is used as a split sample for 13B-0530-C3AS, while 13B-0530-C4BS-C is used as a split sample for 13B-0530-C3BS.



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Table

Table 1 - 2013 Low Resolution Coring Second Supplemental Split Sample Data Comparison Summary

Figures

Figures 1 through 8: Statistical Plots of Dioxin/Furan Concentrations
Figures 9 through 16: Statistical Plots of Pesticide Concentrations

Figures 17 through 27: Statistical Plots of Polychlorinated Biphenyl Concentrations

Figures 28 through 36: Statistical Plots of Polycyclic Aromatic Hydrocarbon Concentrations

Figures 37 through 47: Statistical Plots of Metal Concentrations

Figure 48: Statistical Plot of Total Organic Carbon Concentrations

References

CDM Smith. 2012. Final Quality Assurance Project Plan (QAPP), Addendum No. 10, Low Resolution Coring Second Supplemental Sampling.

Helsel, D.R. 2005. Nondetects and Data Analysis: Statistics for Censored Environmental Data. Wiley-Interscience.

O'Brien, P.C. and T.R. Fleming. 1987. A Paired Prentice-Wilcoxon Test for Censored Paired Data. Biometrics 43: 169-180.



Table 1 2013 Low Resolution Coring Second Supplement Split Sampling Data Comparison Summary Lower Passaic River Study Area

			Comparison Criteria					
Parameter	Number				Statistical Tests			1
		Number of Split	Average Ratio	Percent Difference		alue	.3.03	Overall Split Sample
	of Split	Sample Pairs with	of CPG to EPA				Statistical	Comparison (Same
	Sample	Detected	(for detected	(for detected pairs) (2)	Wilcoxon	Paired Prentice	Difference	or Different) ⁽⁶⁾
	Pairs	Concentrations	pairs) (1)	(101 detected pairs)	Signed Rank test	Wilcoxon	(Yes or No) (5)	
			pa		(3)	test ⁽⁴⁾	(103 01 140)	
Dissing/Furgue						test		
Dioxins/Furans	25	25	4.52 + 2.44	OOV (MACHELE College)	0.007	0.764		D:#*
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	25	25	1.52 ± 3.11	8% (Within Criteria)	0.037	0.761	Yes	Different
1,2,3,4,6,7,8-Heptachlorodibenzofuran	25	25	1.07 ± 0.51	20% (Outside Criteria)	0.201	0.424	No	Same
2,3,7,8-Tetrachlorodibenzo-p-dioxin	25	23	30.98 ± 143.4	26% (Outside Criteria)	0.820	0.525	No	Different
2,3,7,8-Tetrachlorodibenzofuran	25	24	1.19 ± 1.6	13% (Within Criteria)	0.113	0.889	No	Same
Octachlorodibenzo-p-dioxin	25	25	1.74 ± 3.87	4% (Within Criteria)	0.139	0.685	No	Same
Octachlorodibenzofuran	25	24	1.44 ± 1.16	25% (Outside Criteria)	0.284	0.337	No	Different
Total Heptachlorodibenzo-p-dioxin	25	25	1.49 ± 3.14	8% (Within Criteria)	0.008	0.711	Yes	Different
Total Tetrachlorodibenzo-p-dioxin	25	22	4.39 ± 15.59	18% (Outside Criteria)	0.603	0.257	No	Different
Pesticides		1						1
2,4'-dichlorodiphenyldichloroethane (2,4'-DDD)	25	22	0.88 ± 0.31	18% (Outside Criteria)	0.105	0.053	No	Same
2,4'-dichlorodiphenyldichloroethylene (2,4'-DDE)	25	22	1.65 ± 3.57	5% (Within Criteria)	0.051	0.890	No	Same
2,4'-dichlorodiphenyltrichloroethane (2,4'-DDT)	25	9	0.6 ± 0.36	44% (Outside Criteria)	0.044	0.001	Yes	Different
4,4'-dichlorodiphenyldichloroethane (4,4'-DDD)	25	22	0.92 ± 0.33	14% (Within Criteria)	0.144	0.080	No	Same
4,4'-dichlorodiphenyldichloroethylene (4,4'-DDE)	25	23	1.26 ± 1.72	9% (Within Criteria)	0.027	0.986	No	Same
4,4'-dichlorodiphenyltrichloroethane (4,4'-DDT)	25	22	1.62 ± 3.71	59% (Outside Criteria)	0.173	0.024	Yes	Different
alpha-Chlordane	25	23	0.88 ± 0.38	17% (Outside Criteria)	0.004	0.071	No	Same
Dieldrin	25	23	0.83 ± 0.37	26% (Outside Criteria)	0.005	0.008	Yes	Different
Polychlorinated Biphenyls (PCBs)		I		· · · · · · · · · · · · · · · · · · ·			l	L
3,3',4,4'-Tetrachlorobiphenyl (PCB 77)	25	24	2.53 ± 5.46	17% (Outside Criteria)	0.089	0.119	No	Different
3,4,4',5-Tetrachlorobiphenyl (PCB 81)	25	15	1.98 ± 3.31	13% (Within Criteria)	0.065	0.132	No	Same
2,3,3',4,4'-Pentachlorobiphenyl (PCB 105)	25	24	1.58 ± 2.55	13% (Within Criteria)	0.184	0.235	No	Same
2,3,4,4',5-Pentachlorobiphenyl (PCB 114)	25	22	1.81 ± 3.32	14% (Within Criteria)	0.050	0.128	No	Same
2,3',4,4',5-Pentachlorobiphenyl (PCB 118)	25	24	1.58 ± 2.47	8% (Within Criteria)	0.149	0.231	No	Same
2',3,4,4',5-Pentachlorobiphenyl (PCB 123)	25	23	1.72 ± 3.13	9% (Within Criteria)	0.207	0.264	No	Same
3,3',4,4',5-Pentachlorobiphenyl (PCB 126)	25	12	1.72 ± 3.13 1.26 ± 0.49	25% (Outside Criteria)	0.170	0.204	Yes	Different
2,3,3',4,4',5-Hexachlorobiphenyl (PCB 156) +	23	12	1.20 ± 0.49	25% (Outside Criteria)	0.170	0.040	res	Different
2,3,3',4,4',5'-Hexachlorobiphenyl (PCB 157)	25	24	1.95 ± 3.52	13% (Within Criteria)	0.003	0.048	Yes	Different
2,3',4,4',5,5'-Hexachlorobiphenyl (PCB 167)	25	23	1.92 ± 3.71	9% (Within Criteria)	0.009	0.077	No	Same
2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB 189)	25	22	1.92 ± 3.71 1.8 ± 3.45	9% (Within Criteria)	0.661	0.077	No	Same
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Total PCBs	25	25	1.39 ± 1.55	8% (Within Criteria)	0.024	0.189	Yes	Different
Polycyclic Aromatic Hydrocarbons (PAHs)	25	35	107 117	400/ (Outside Criteria)	0.044	0.076	Vac	Different
Anthracene	25	25	1.07 ± 1.17	40% (Outside Criteria)	0.041	0.076	Yes	Different
Benzo(a)anthracene	25	24	0.86 ± 0.43	38% (Outside Criteria)	0.027	0.017	Yes	Different
Benzo(a)pyrene	25	25	0.92 ± 0.39	28% (Outside Criteria)	0.197	0.099	No	Same
Chrysene	25	23	0.94 ± 0.4	26% (Outside Criteria)	0.166	0.095	No	Same
Fluoranthene	25	24	0.81 ± 0.39	33% (Outside Criteria)	0.008	0.005	Yes	Different
Indeno(1,2,3-cd)pyrene	25	25	0.74 ± 0.28	36% (Outside Criteria)	0.003	0.002	Yes	Different
Naphthalene	25	22	1.01 ± 0.86	50% (Outside Criteria)	0.217	0.166	No	Same
Phenanthrene	25	24	1.18 ± 0.9	29% (Outside Criteria)	0.247	0.177	No	Same
Pyrene	25	24	0.79 ± 0.37	38% (Outside Criteria)	0.008	0.005	Yes	Different
Metals		1	,				T	T
Arsenic	25	25	1.15 ± 1.24	16% (Within Criteria)	0.989	0.454	No	Same
Barium	25	25	1.3 ± 0.88	12% (Within Criteria)	0.135	0.093	No	Same
Cadmium	25	20	4.11 ± 11.54	30% (Outside Criteria)	0.002	0.021	Yes	Different
Chromium	25	25	1.7 ± 3.06	4% (Within Criteria)	0.034	0.122	Yes	Different
Cobalt	25	25	1.21 ± 0.7	4% (Within Criteria)	0.045	0.117	Yes	Same
Copper	25	25	1.46 ± 1.99	12% (Within Criteria)	0.184	0.321	No	Same
Iron	25	25	1.13 ± 0.63	4% (Within Criteria)	0.989	0.468	No	Same
Lead	25	25	1.6 ± 1.39	16% (Within Criteria)	<0.001	0.004	Yes	Different
Nickel	25	25	1.1 ± 0.75	8% (Within Criteria)	0.572	0.933	No	Same
Zinc	25	25	1.31 ± 1.23	8% (Within Criteria)	0.106	0.114	No	Same
Mercury	25	25	2.18 ± 3.86	32% (Outside Criteria)	0.001	0.066	Yes	Different
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Organic Carbons								

Results outside acceptance criteria are **bolded**.

Notes:

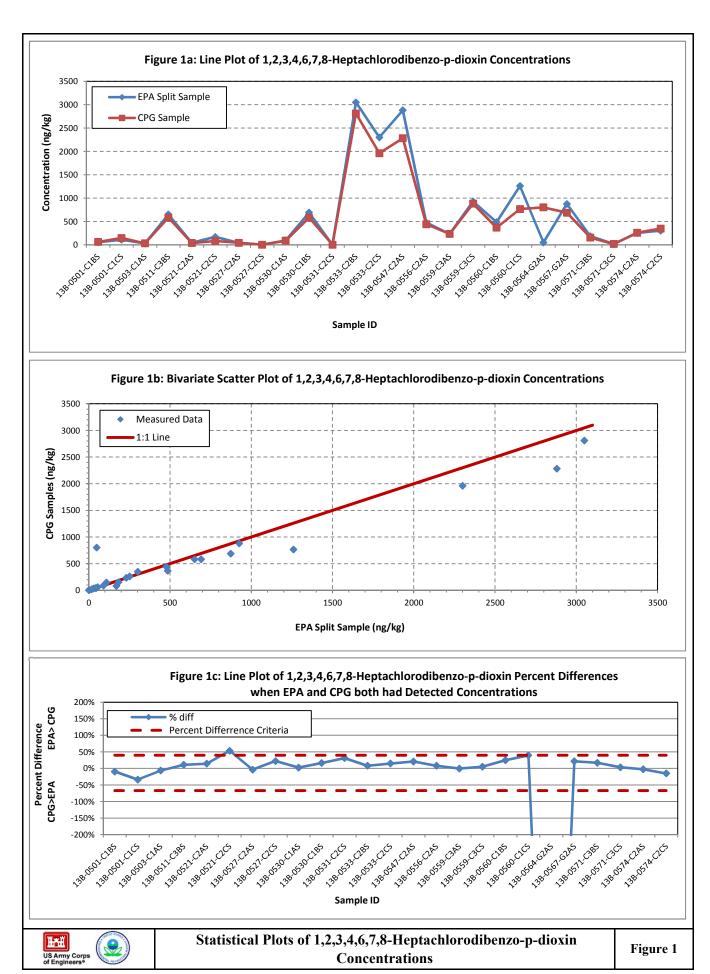
- (1) Average ratio (criteria: 0.70-1.30) with standard deviation .
- (2) Percent difference criteria: no more than 16% of split samples outside of -67 to 40 percent difference.
- (3) Wilcoxon Signed Rank test was employed at significance level (p) of 0.05.
- (4) Paired Prentice Wilcoxon test was employed at significance level (p) of 0.05.
- (5) Statistical difference was based on Paired Prentice Wilcoxon test when they are at least one nondetected concentration. Otherwise, it was based on Wilcoxon Signed Rank test to handle potential outliers.
- (6) If there are at least two of the three criteria (average ratio, percent different and statistical difference) met, the overall split sample comparison would be labeled "same". Otherwise, it would be "different".

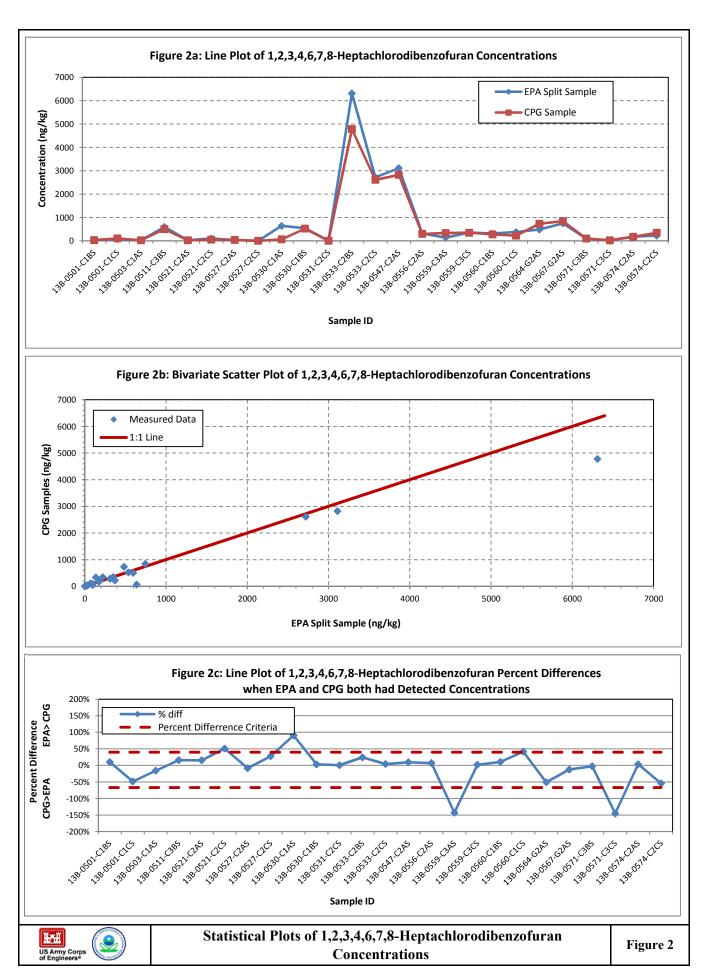
Abbreviations:

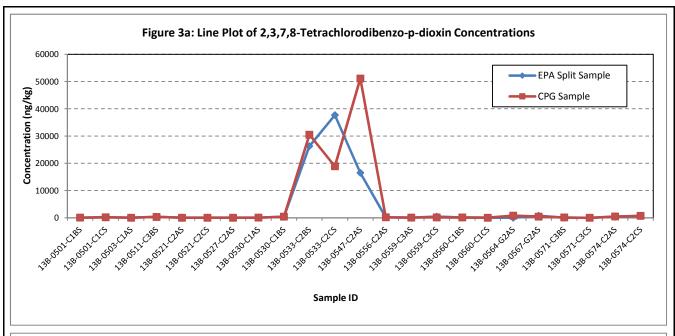
CPG = Cooperating Parties Group

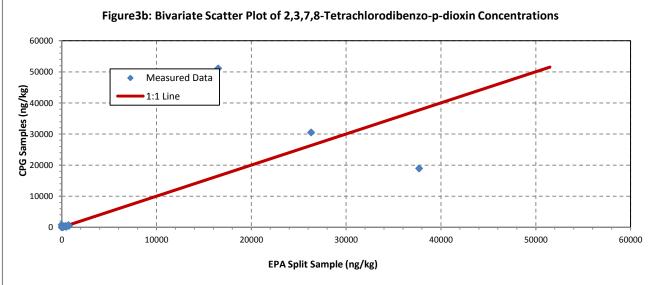
EPA = United States Environmental Protection Agency

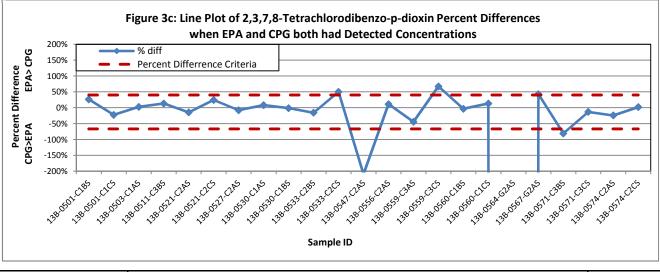


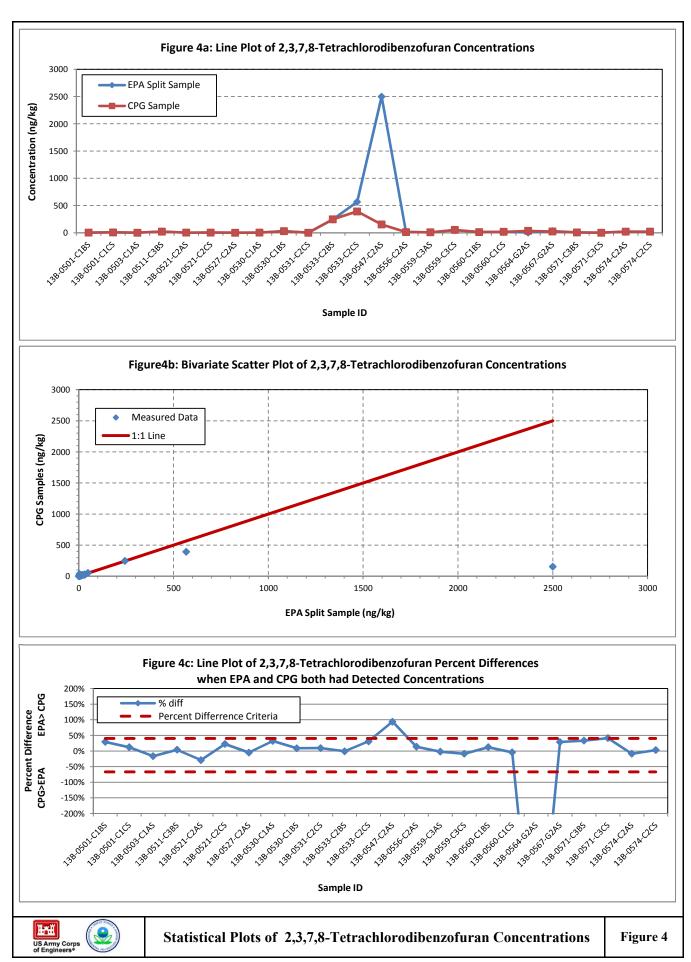


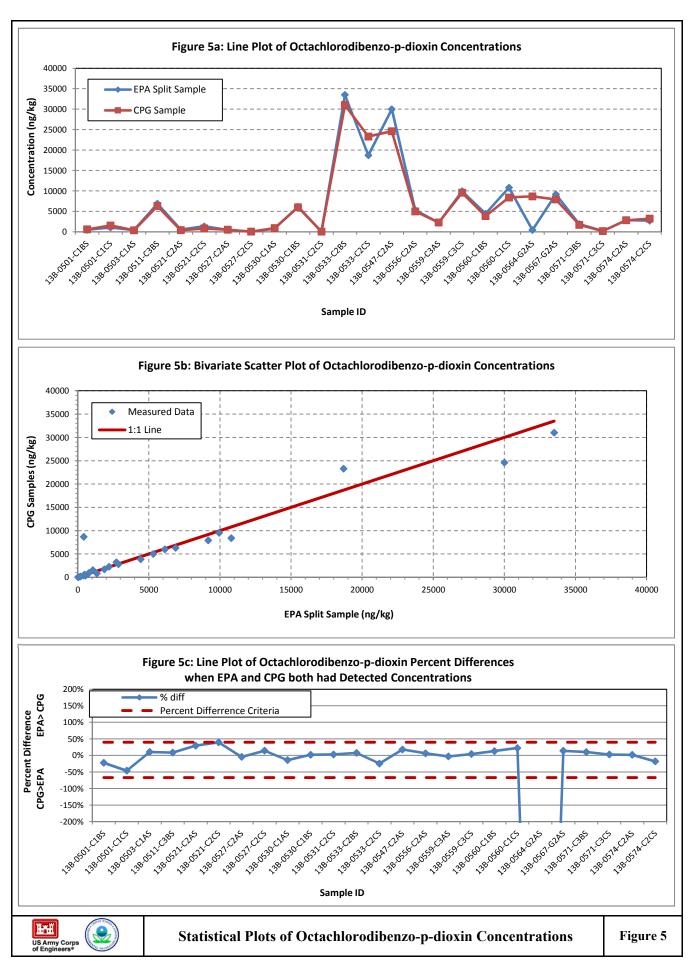


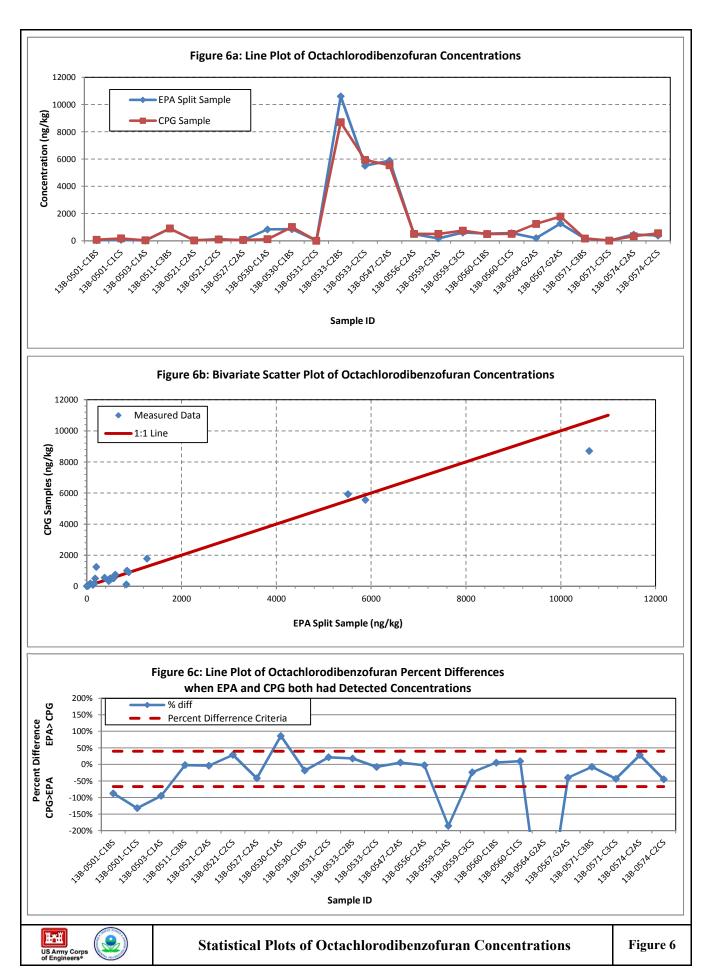


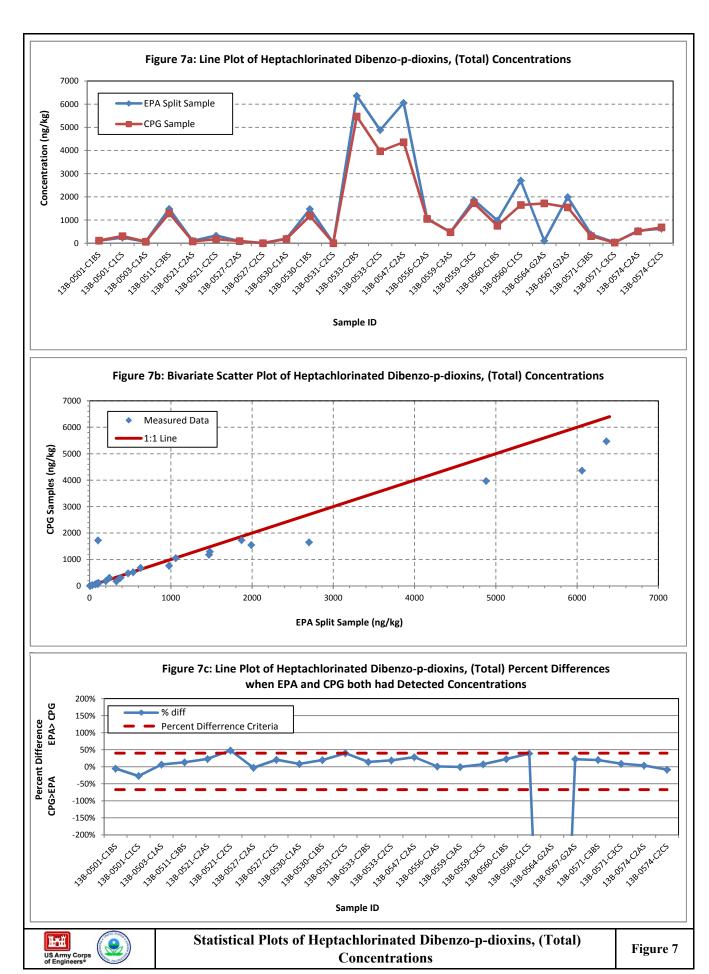


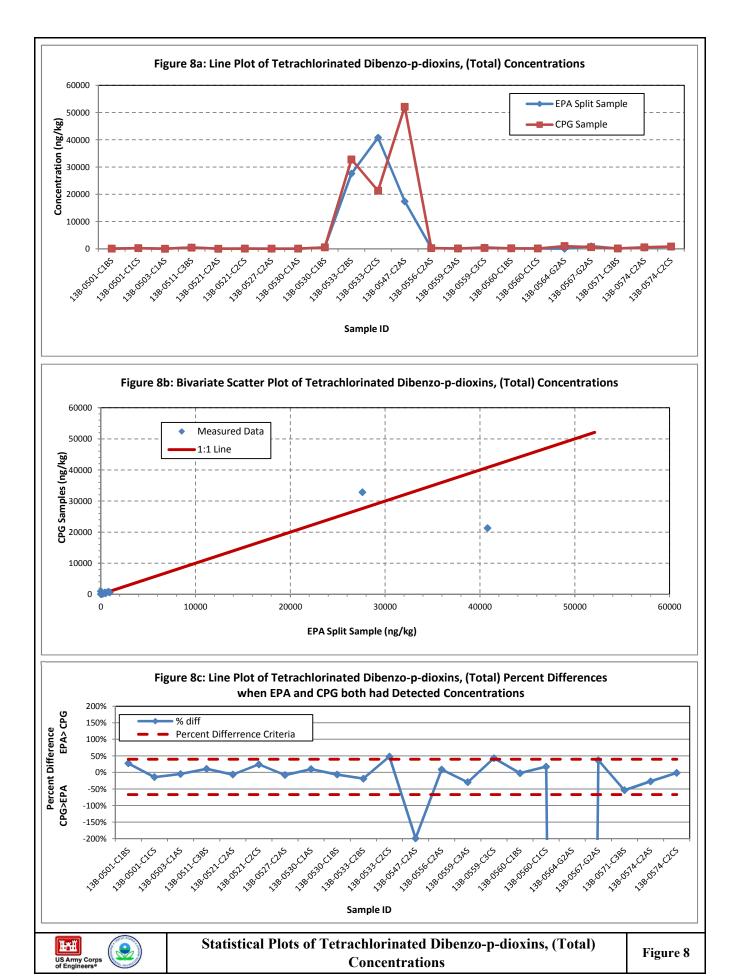


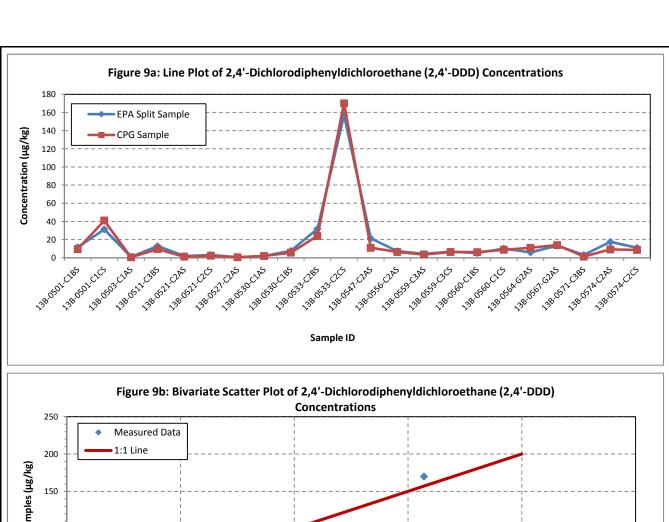


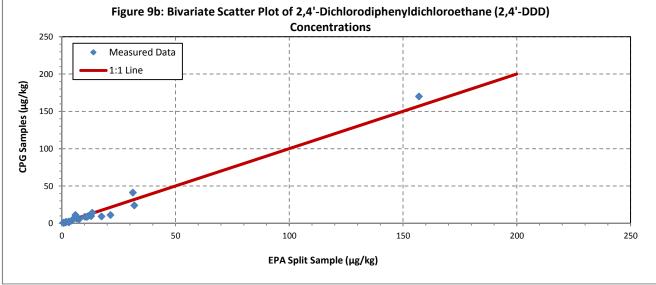


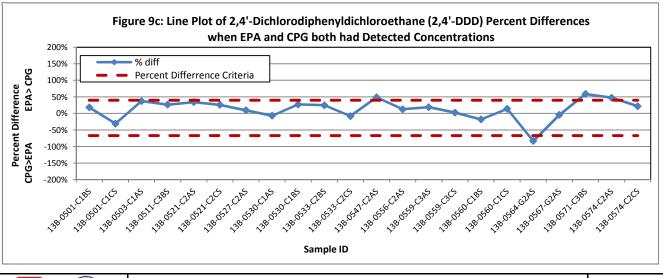






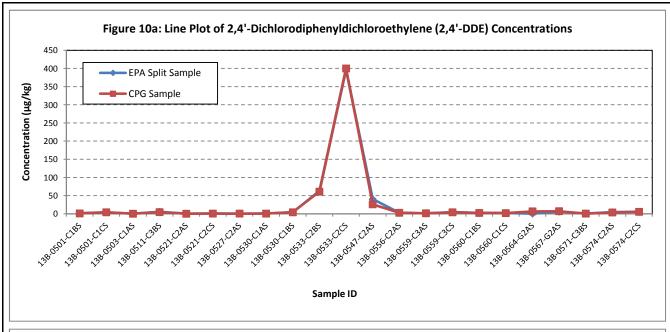


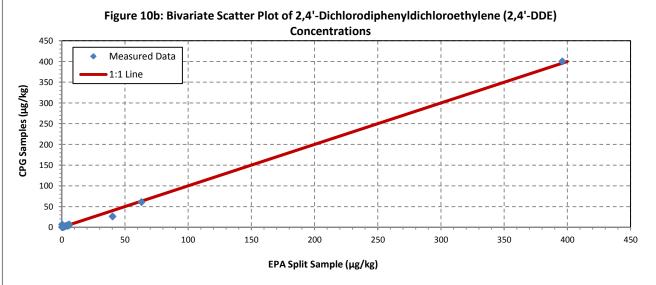


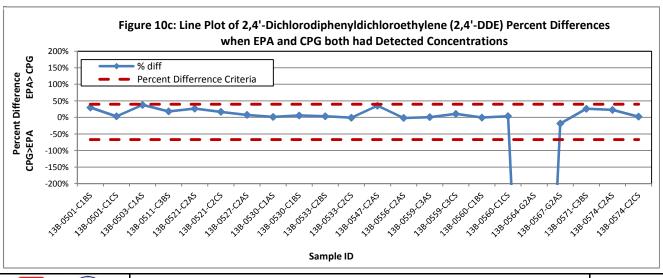


Statistical Plots of 2,4'-Dichlorodiphenyldichloroethane (2,4'-DDD)

Concentrations

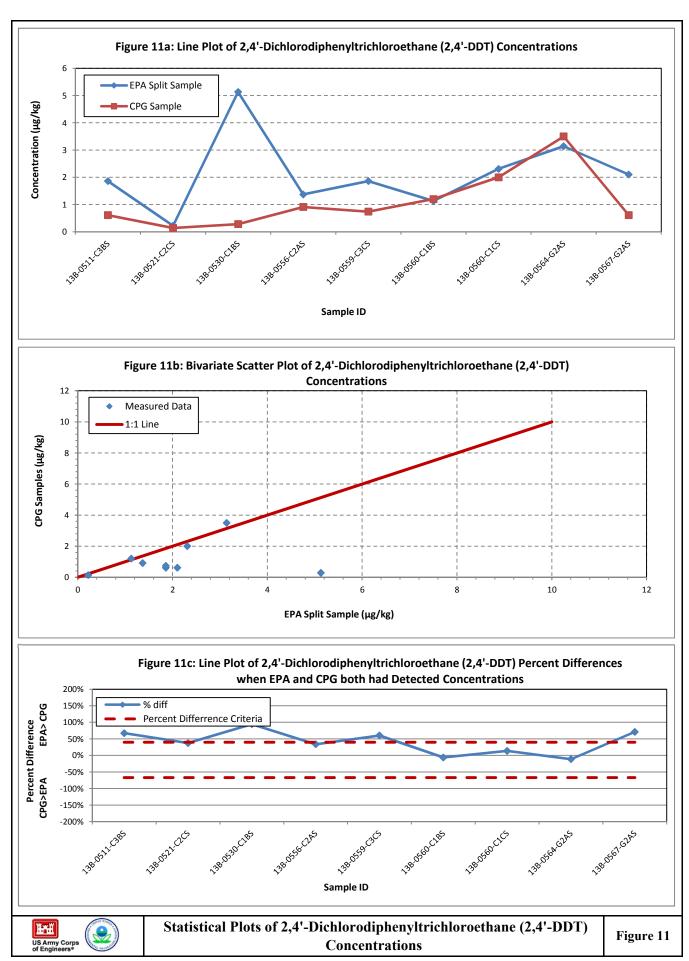


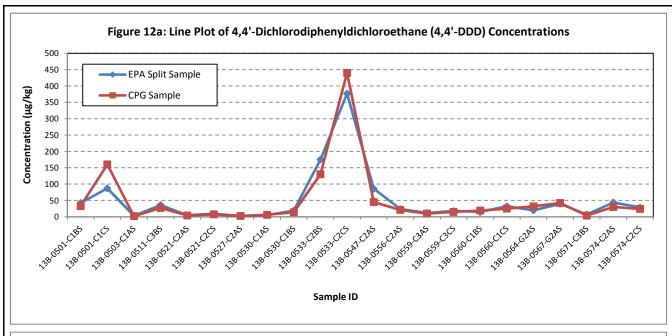


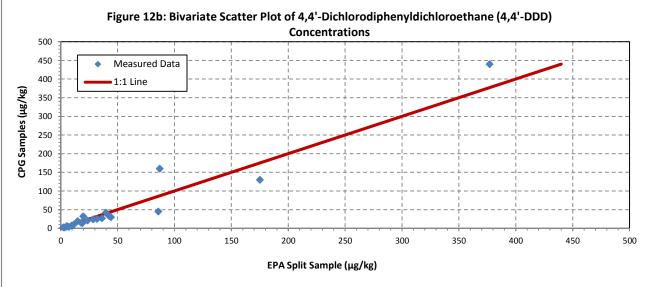


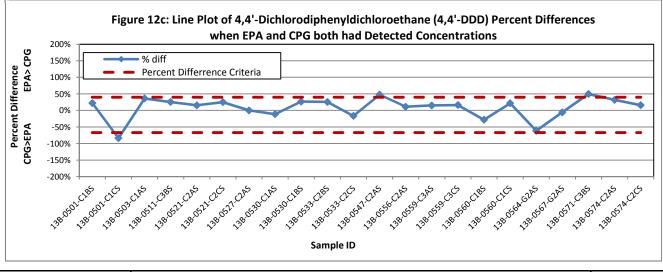
US Army Corps of Engineers®

Statistical Plots of 2,4'-Dichlorodiphenyldichloroethylene (2,4'-DDE) Concentrations





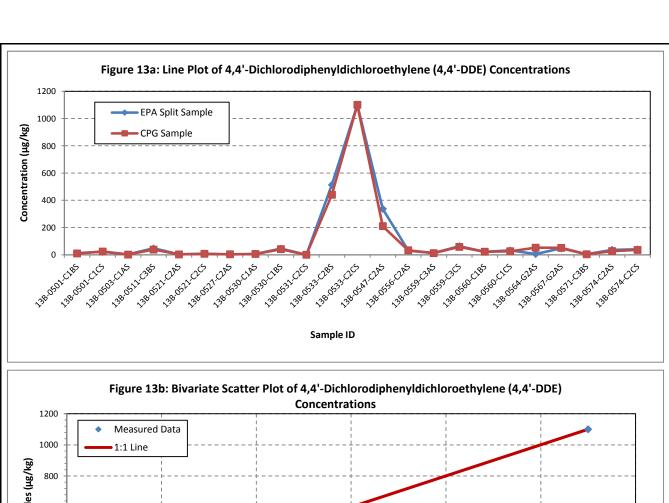


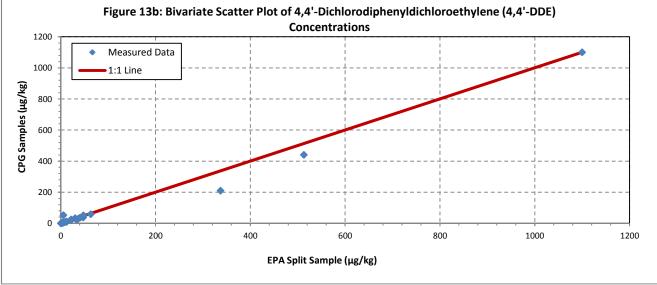


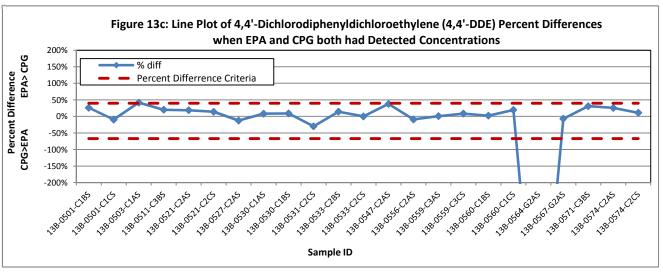


Statistical Plots of 4,4'-Dichlorodiphenyldichloroethane (4,4'-DDD)

Concentrations

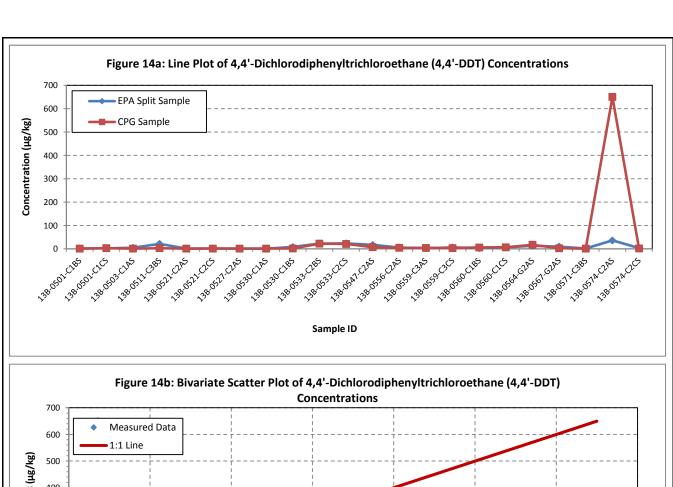


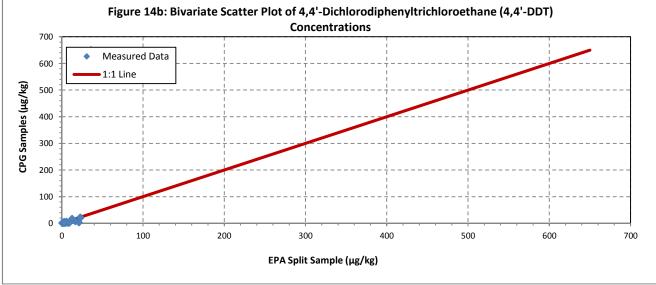


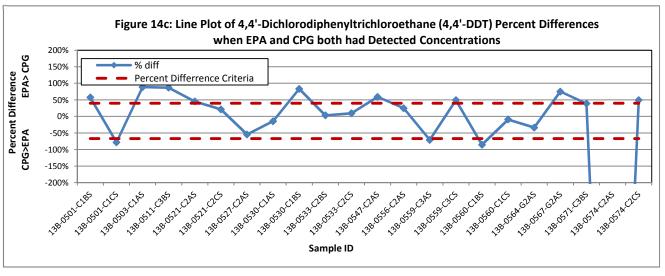


Statistical Plots of 4,4'-Dichlorodiphenyldichloroethylene (4,4'-DDE)

Concentrations

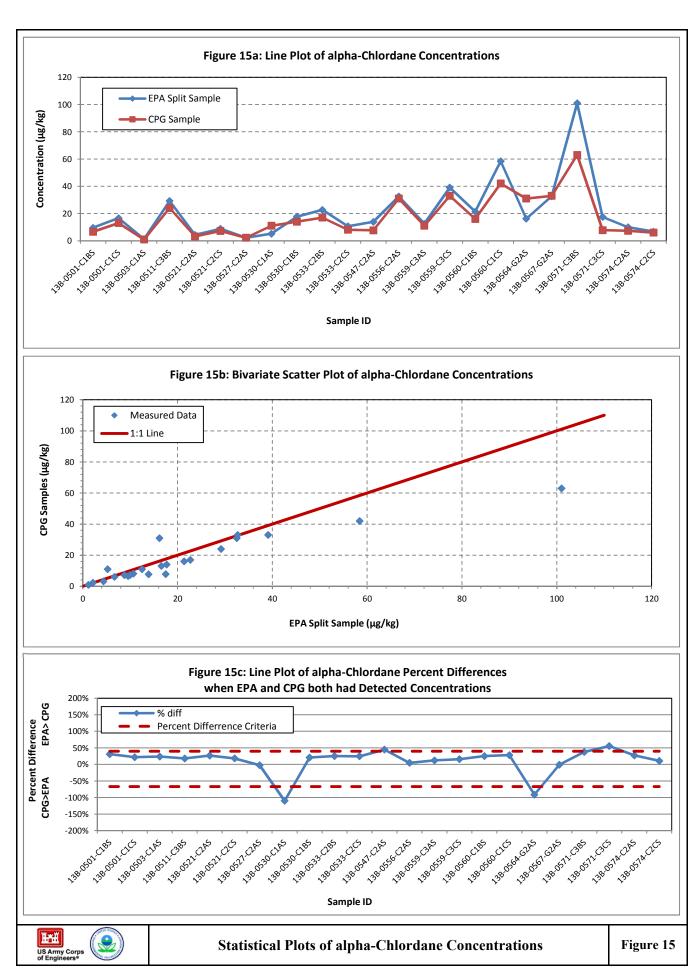


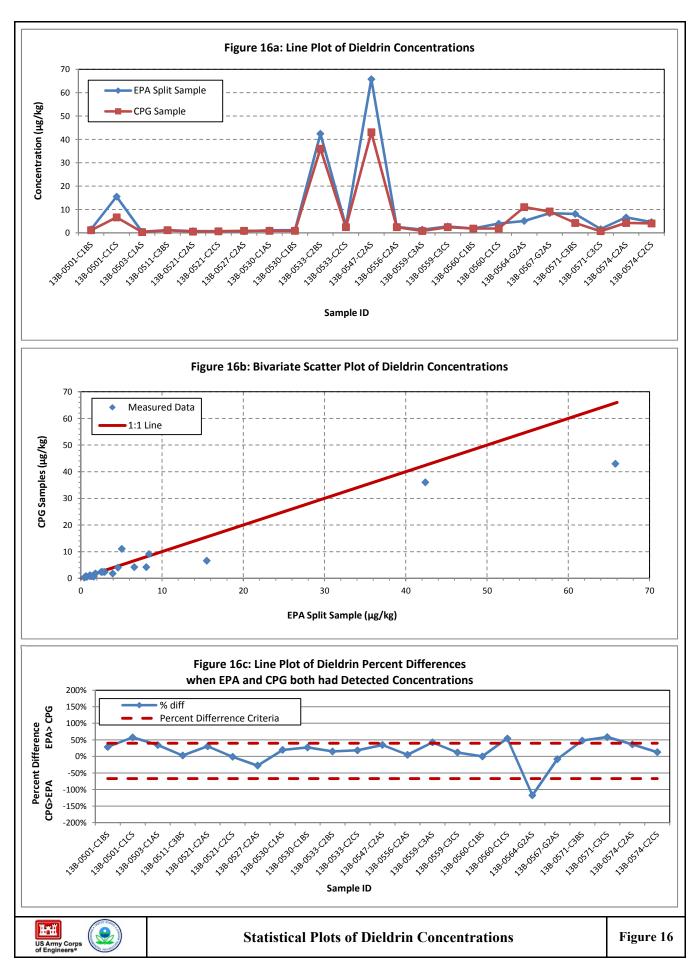


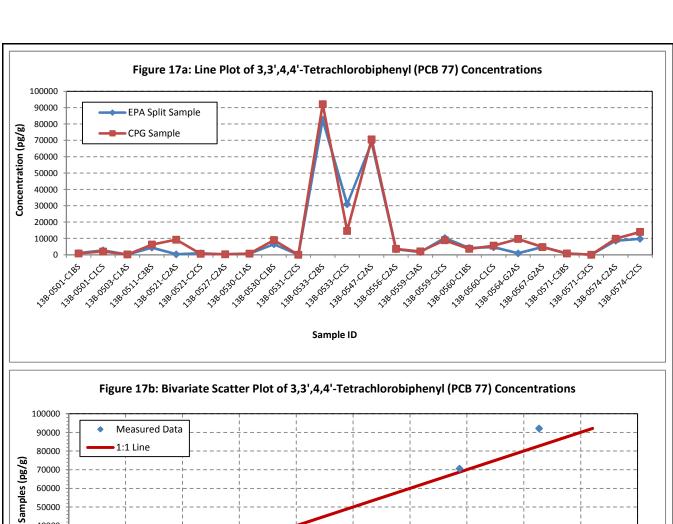


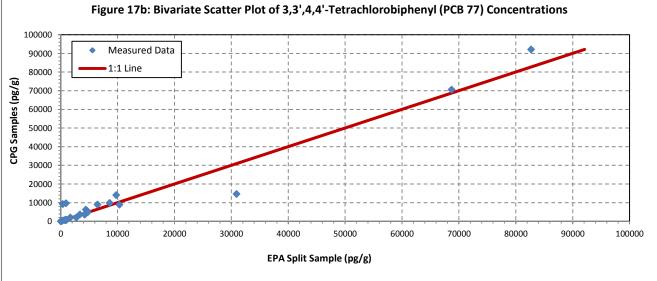
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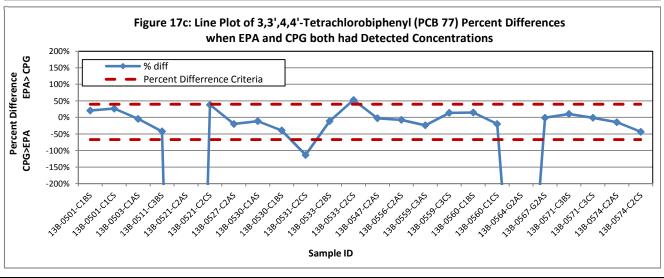
Statistical Plots of 4,4'-Dichlorodiphenyltrichloroethane (4,4'-DDT) Concentrations



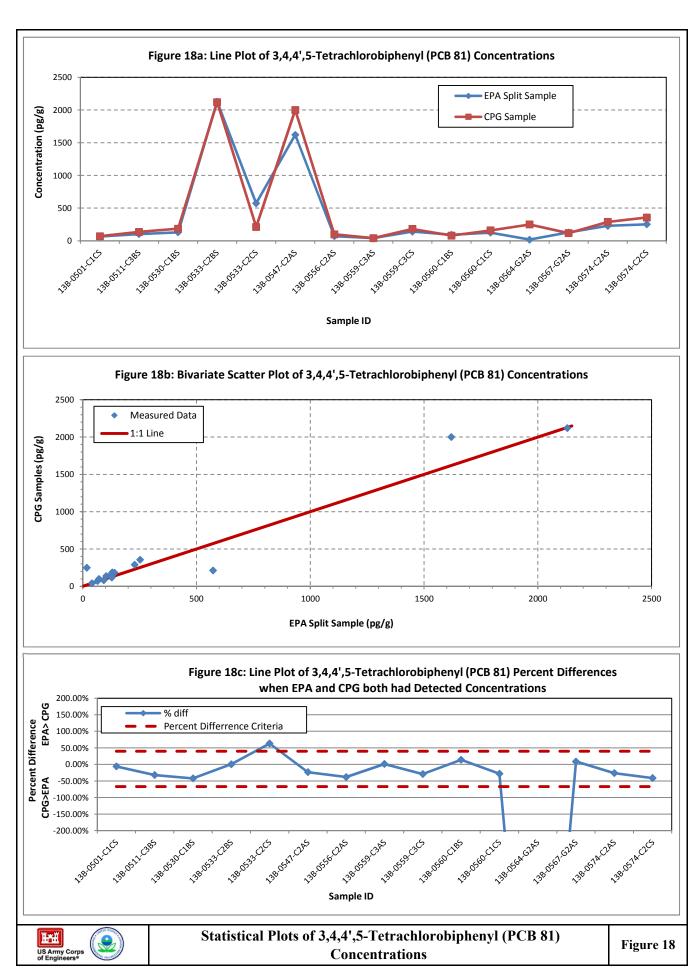


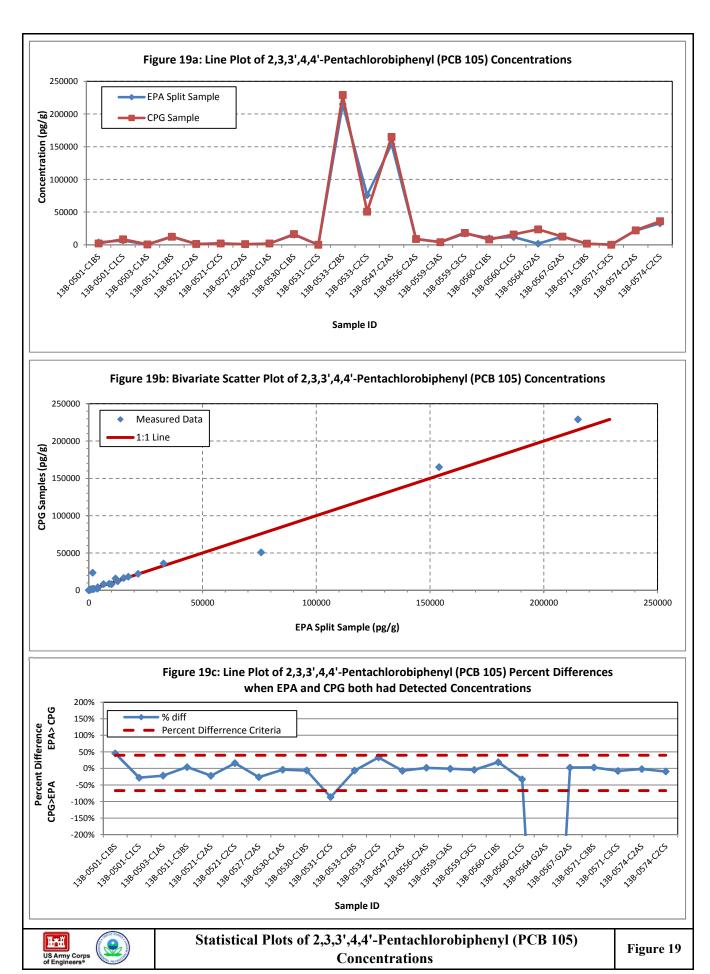


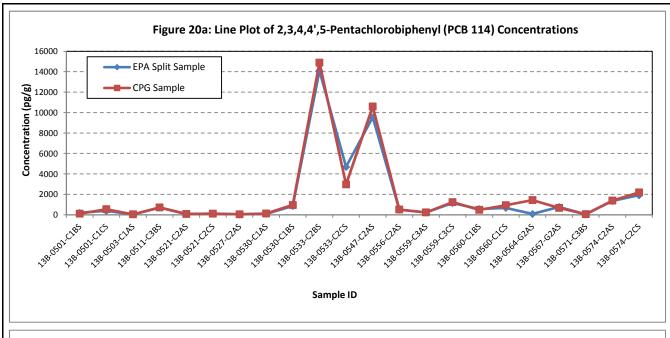


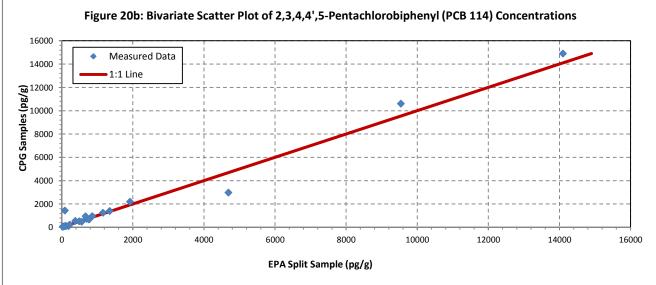


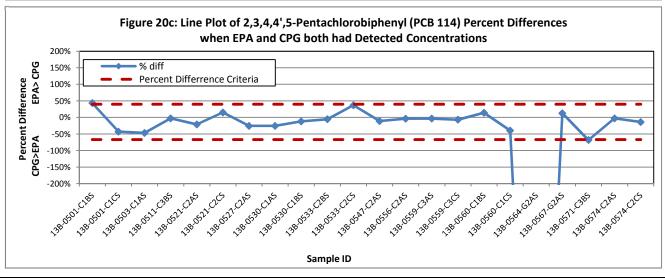
H-H US Army Corps of Engineers®

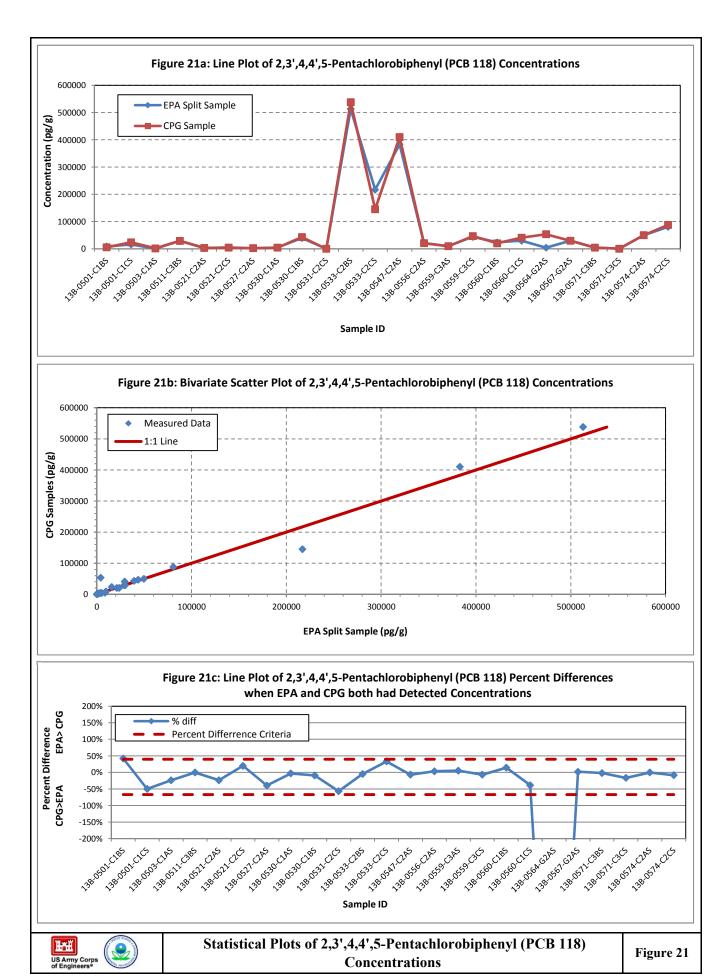


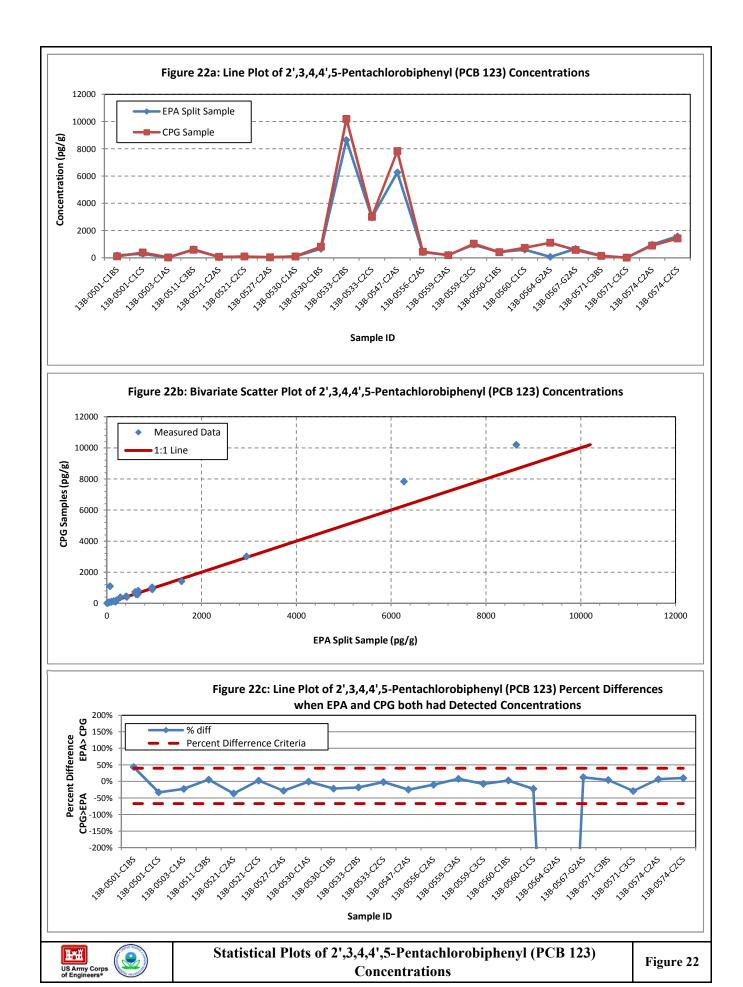


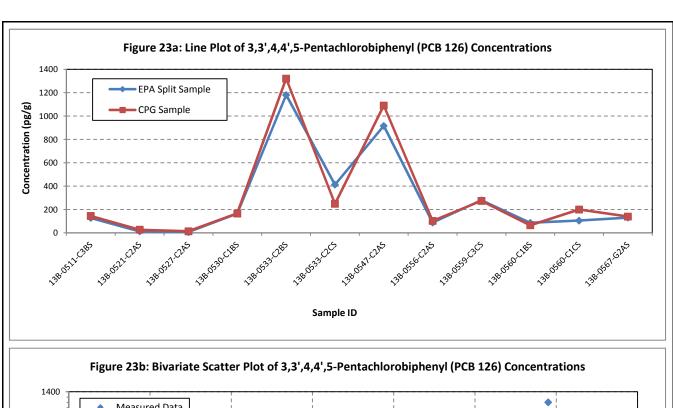


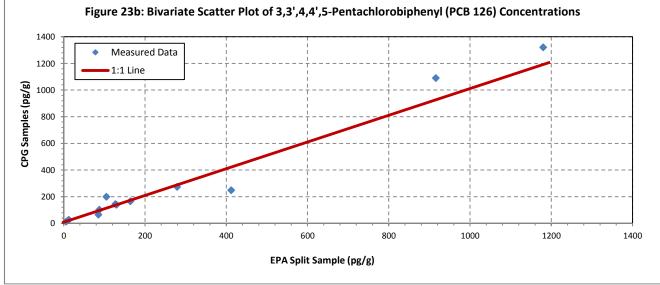


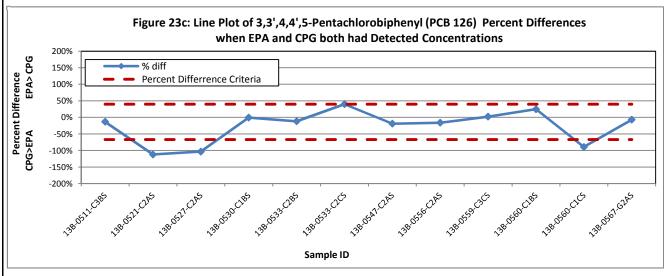














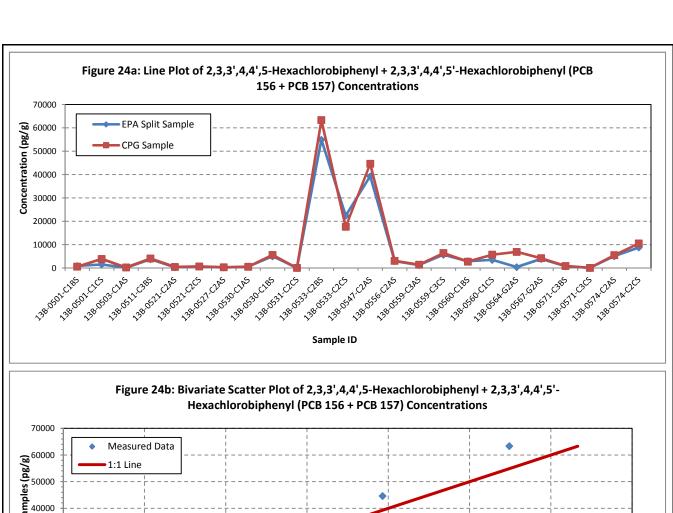


Figure 24b: Bivariate Scatter Plot of 2,3,3',4,4',5-Hexachlorobiphenyl + 2,3,3',4,4',5'Hexachlorobiphenyl (PCB 156 + PCB 157) Concentrations

70000

Measured Data

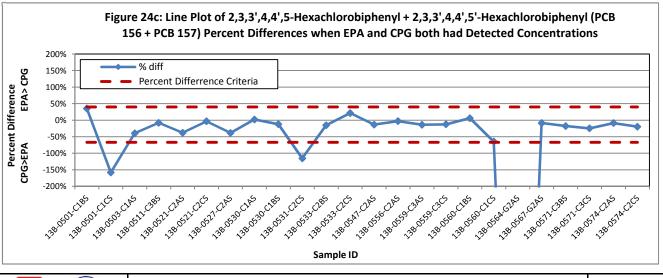
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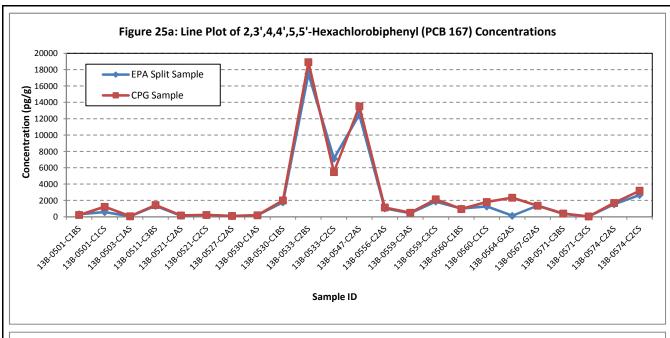
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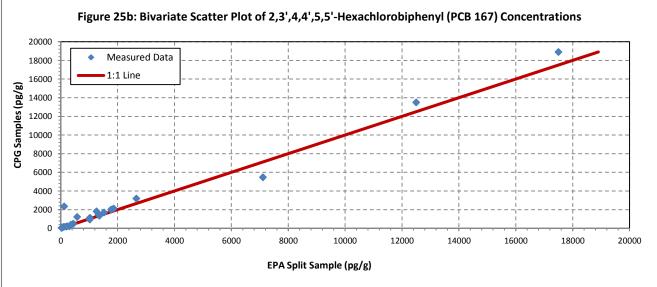
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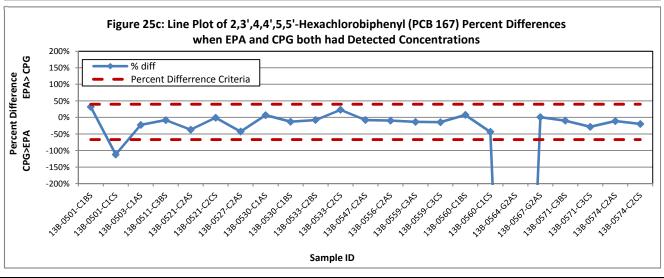
10000

EPA Split Sample (pg/g)



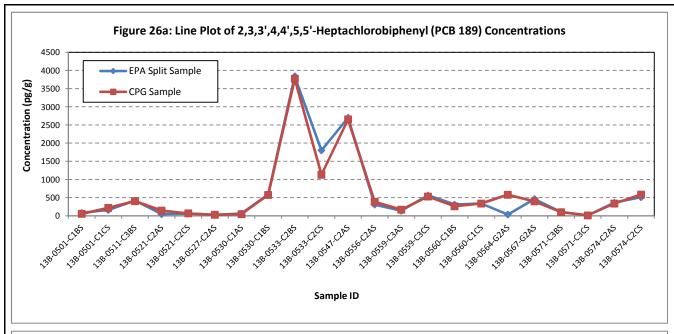


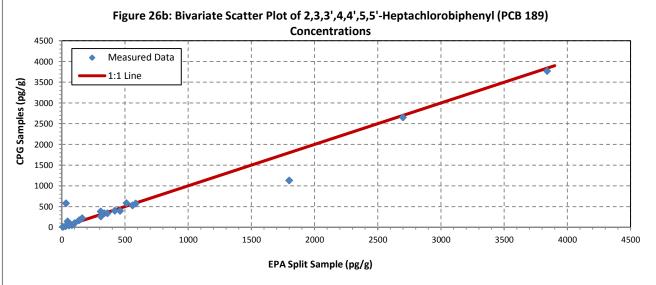


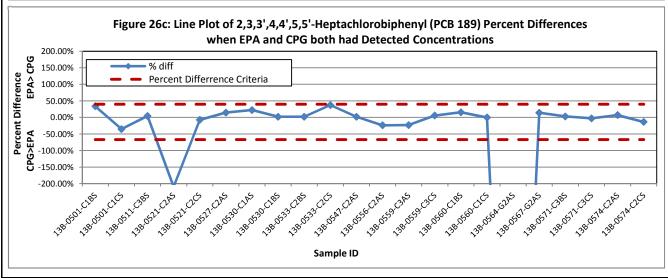




Statistical Plots of 2,3',4,4',5,5'-Hexachlorobiphenyl (PCB 167) Concentrations







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Statistical Plots of 2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB 189) Concentrations

